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| 14. ABSTRACT (Cholesteryl)benzoateethynylene oligomers having 3, 5 and 7 repeat units and the homologue polymer were synthesized by a divergence-convergence approach by the Sonogashira-Heck reaction. Their chemical structure was analyzed by 1H, 13C NMR, UV-Vis, fluorescence spectroscopy and circular dichroism. X-Ray diffraction patterns of all the materials show only a first order peak at 2.05° in 2 \square, indicative of a lamellar order within a distance of 4.3 nm. This is twice the calculated distance of a molecule in its more extended conformation, i.e. of 2.15 nm, and is consistent with a disordered Smectic A phase for the trimer and pentamer and a nematic phase for the heptamer and polymer. The most probable model of organization corresponds to a supramolecular assembly in bilayers, where the cholesteryl chains are oriented in an opposite sense, i.e. in a back-to-back "comb like" fashion. Since the molecular shape of the materials is consistent with brick or board-like structures and the molecules are stacked in blocks randomly oriented, the (cholesteryl)benzoateethynylene materials could be described as Sanidic LCs as a general term to classify their mesomorphic behavior. Optical properties are discussed in terms of the conjugation length and the terminal groups, iodine or in one case, hydrogen. In general the results confirm that all the molecules assume in solution a more planar conformational geometry when passing from the ground to the excited state. Circular dichroism spectra measured were consistent with the observed structural properties. | | | | | |
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Final Report

**Synthesis of Chromophores Extension for
Nonlinear Optics Applications**

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SYNTHESIS OF CHROMOPHORES EXTENSION FOR NONLINEAR OPTICS APPLICATIONS

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Grant Objectives: no changes.

Status of Effort: all research objectives have been met.

Summary: (Cholesteryl)benzoateethynylene oligomers having 3, 5 and 7 repeat units and the homologue polymer were synthesized by a divergence-convergence approach by the Sonogashira-Heck reaction. Their chemical structure was analyzed by ^1H , ^{13}C NMR, UV-Vis, fluorescence spectroscopy and circular dichroism. X-Ray diffraction patterns of all the materials show only a first order peak at 2.05° in 2θ , indicative of a lamellar order within a distance of 4.3 nm. This is twice the calculated distance of a molecule in its more extended conformation, i.e. of 2.15 nm, and is consistent with a disordered Smectic A phase for the trimer and pentamer and a nematic phase for the heptamer and polymer. The most probable model of organization corresponds to a supramolecular assembly in bilayers, where the cholesteryl chains are oriented in an opposite sense, i.e. in a back-to-back “comb like” fashion. Since the molecular shape of the materials is consistent with brick or board-like structures and the molecules are stacked in blocks randomly oriented, the (cholesteryl)benzoateethynylene materials could be described as Sanidic LCs as a general term to classify their mesomorphic behavior. Optical properties are discussed in terms of the conjugation length and the terminal groups, iodine or in one case, hydrogen. In general the results confirm that all the molecules assume in solution a more planar conformational geometry when passing from the ground to the excited state. Circular dichroism spectra measured were consistent with the observed structural properties.

Accomplishments:

Molecules that were synthesized per the grant. The synthesis of the oligomers and the homologue polymer was carried out by applying the bidirectional divergent/convergent approach. The strategy consisted in obtaining three bi-functional monomers **6**, **8** and **10** in large amounts. Then, by their selective reaction by the step by step approach, the oligomers were constructed. The synthesis of the first monomers was started by the conversion of the aniline to a triazene group, Scheme 1, from the commercially available **1** by a pathway that involves the preparation of the intermediary diazonium cation **2**, which is obtained in quantitative yields (97 %) by a modification of the Schiemann reaction. Diazonium cation **2** is stable and can be isolated by suction filtering. After its dissolution in a mixture of cold DMF and diethylamine, the triazene **3**

was obtained in 66 % yielding. DCC-mediated esterification of **3** with cholesterol in dry and free of methanol CH_2Cl_2 gave **4** in 67 % yield. Then, TMSA was Pd/Cu cross-coupled to **4** in triethylamine. The acetylene protected monomer **5** was obtained in 95 % yield, which, after its desilylation with TBAF, led to the bi-functional monomer **6** in 99 % yield.

The second monomer **8** was obtained by DCC-esterification conditions of the commercial acid **7** with cholesterol in CH_2Cl_2 , Scheme 2. Then, one portion of **7** was cross-coupled with TMSA under the Heck reaction conditions to afford **9**, from which the third bi-functional monomer **10** was obtained after desilylation in 98% yield.

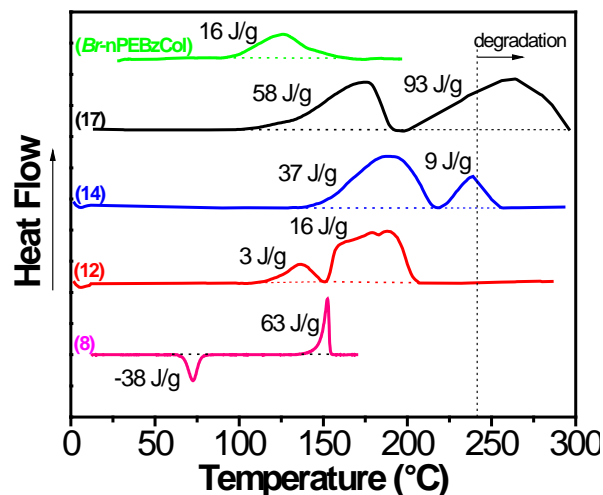
The bidirectional synthesis of the oligomer series involved two sets of reactions depicted in Scheme 3. Starting from **8** as the core, the oligomers were grown in odd numbers. Initially, two equivalents of **6** are Pd cross-coupled with **8** to obtain **11**. The conversion of the triazeno group to the iodine group of **11** was carried out with iodomethane in a sealed capsule under vacuum. It is worth mentioning that iodomethane is not a good solvent for **11**, as well as for longer triazene terminated oligomers, most likely due to the organogelator property of the steroid cholesteryl group. However, the iodine terminated oligomers can be easily isolated from the unreacted triazene terminated oligomers by flash chromatography because of their fairly different retention factors. The elution of the iodine terminated oligomers can be followed by irradiating the chromatography column with the 365 nm radiation of an UV lamp since they fluoresce while the triazene terminated oligomers do not. The trimer **12** is obtained in 86 % yield after been purified by silica chromatography and then by preparative GPC chromatography (Biorads, Bio-Beds SX1, chloroform). As **12** is terminated with iodides, the next Pd cross-coupling with two equivalents of **6** gives the triazene terminated pentamer **13** in 75 % yields. Iodination of **13** afforded the iodide terminated pentamer **14**, which was divided in two fractions. The first fraction was Pd cross-coupled with two equivalents of (cholesteryl) 3-ethynyl benzoate monomer to obtain the hydrogen terminated heptamer **15**. The second fraction of **14** was Pd cross-coupled with two equivalents of **6** to generate the triazene terminated heptamer **16**, from which the heptamer **17** is obtained after iodination in 41 % yield. Indeed, this route of synthesis is very practical because molecules grow at each step and the only byproduct is the diacetylene dimer of **6** in small amount, which is eliminated during the work up process or by the preparative GPC chromatography. The polymer **Br-nPEBzCol** was synthesized by reacting 1 equivalent of **10** with 1.1 equivalents of **8** under the Sonogashira-Heck reaction conditions, using only Et_3N as solvent. The polymer was purified by precipitation in methanol and then by preparative GPC to obtain a pale yellow solid. According to gel permeation chromatography (GPC) using PS standards, the calculated average molecular weight was of 23,715 Da with a polydispersity index (PDI) of 3.21.

The chemical structure of all molecules was confirmed by ^1H and ^{13}C NMR. All the molecules including the polymer **Br-nPEBzCol** are very soluble in chloroform, CH_2Cl_2 , THF and precipitate in methanol, acetone and acetonitrile. Interestingly, we note that all the molecules form a gel in toluene.

Thermal properties and solid state organization. The thermogravimetric analysis showed that oligomers are thermally stable up to ca. 240 °C, an exponential degradation then occurs by a shout down of mass loss. A drastic colour change from pale yellow to deep brown-black is observed at this temperature by POM. In the case of the polymer, we observed a weight loss of 2 % at 130 °C, which increases and becomes faster after 180 °C as has been reported for other PE polymers. The weight loss is attributed to the possible low molecular weight fractions as well as to the remaining monomer, water and traces of solvent.

We note that none of the oligomers or polymer showed any exothermic crystallization peak in the first cooling cycle or any fusion peak in the second heating cycle, see the DSC figure.

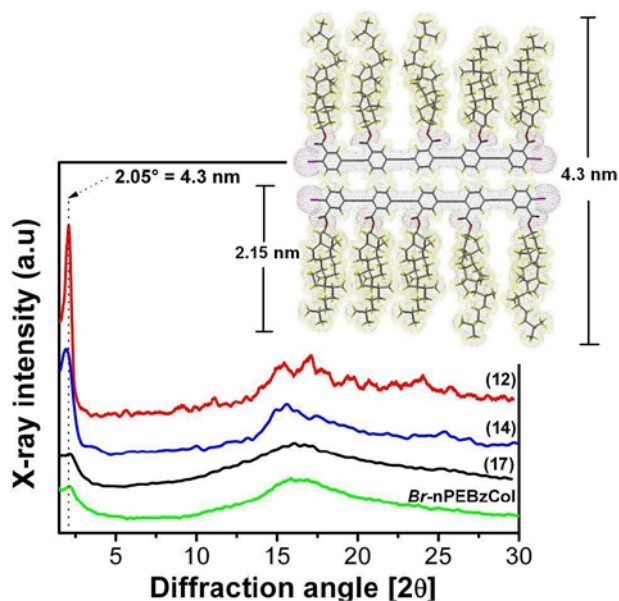
As observed by POM, samples in the partially melted state took more than four hours to get to the solid state. Interestingly, monomer **8** that shows the highest fusion enthalpy exhibits a crystallization transition before melting, while no exothermic peak was observed in the cooling cycle. Furthermore, by POM and during heating, a cholesteric texture with oily streaks was observed in a quite limited temperature interval of ca. 5 °C at 165-170 °C and just after keeping this temperature for about 30 min. On the contrary, **12**, **14** and **17** show two broad fusion transitions.



Although the development of any known texture reported in the literature i.e., smectic, cholesteric or nematic was not evidenced, the materials at these temperatures are strongly birefringent, which suggests the existence of a mesomorphic order. In contrast, the second transition peak for **14** and **17** somewhat coincides with the beginning of degradation (or/and cross-linking) close to 240 °C as determined by TGA. In particular, for these oligomers their total fusion was never observed by POM because of their tendency to develop a deep brown colour at high temperature. The low fusion enthalpy of 16 J/g of the polymer is attributed to lower molecular moieties such as the presence of dimers, because no fusion was observed by POM at higher temperatures.

The X-ray diffraction patterns of **12**, **14**, **17** and *Br-nPEBzCol* at room temperature are presented in the following figure. In general, it can be observed that: i) all the diffraction patterns present only a first ordered peak of 2.05° in 2θ indicative of a lamellar system with a distance therein of 4.3 nm, ii) this lamellar peak becomes wider and less intense as the oligomer's length is increased, iii) at higher angles, a single but broad band (2θ = 15-18°) is observed with an average distance of 0.55 nm, which is associated with the distance between the cholesteryl chains and iv) very weak and diffuse diffraction peaks are presented mainly with the trimer and the pentamer at 2θ = 25-26°, with an average distance of 0.34 nm assigned to the distance between the phenyls of conjugated chains. From these observations, one can assume that all of the molecules are arranged in bi-layers, since the phenyl-to-cholesteryl distance in their most

extended conformation is of only 2.15 nm. Moreover, and in agreement with what is found by theoretical simulation, the supramolecular arrangement can be compared with two back-to-back superposed combs, where the cholesteryl chains are oriented in opposite directions. The X-ray diffraction pattern of both trimer **12** and pentamer **14** is characteristic of a disordered Smectic phase; in the small angle region only one sharp reflection (d_{001}) is observed, while in the wide angle region several reflections overlap with a broad band indicative of a high local ordering of the cholesteryl chains. At least for the pentamer **14** a possible “cybotactic columnar phase” could be manifested, where the phase is composed of cybotactic groups of tail-to-tail, and columnar because from the X-ray data there is long range (within the groups) order in two dimensions; smectic layer order of the cholesterol side chains (0.45 nm), and smectic layer order of the PPE chains (0.33 nm) in an orthogonal direction. The X-ray diffraction patterns recorded for the heptamer **17** and the polymer **Br-nPEBzCol** are typical of a nematic or cholesteric phase since they contain only a diffuse band in both the small and wide angle region. However, a cholesteric phase is not possible since there are too many cholesteryls to favour an ordered rotation around the long axis of the molecule and because of the presumed strong π - π interaction between the conjugated backbones, which impedes it. We therefore suggest a nematic type mesophase for **17** and the polymer. In general, the molecules are assembled in bilayers and aggregated into lamellae, which can be brick-like visualized. Additionally, temperature dependant X-ray diffraction investigations of the materials showed no change in the Bragg’s peak or the appearance of other mesophases as function of the temperature. On the basis of all of the results, we concluded that the term Sanidic LC phase could be used to describe the mesomorphic behaviour of these conjugated materials. This term has been proposed by other authors for other PPE’s.

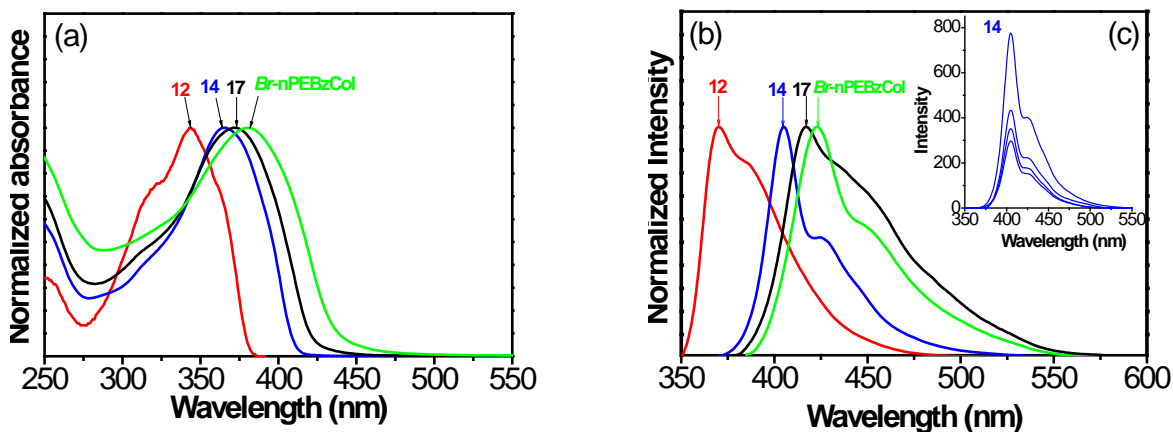


Optical properties. All the optical properties in chloroform solution are collected in the following table. The optical data of (11-undecanol)benzoate PE heptamer and of a cholesteryl hydrogen terminated heptamer **15** are included for comparison. The UV-Vis spectra of the cholesteryl iodine terminated oligomer series and of the homopolymer in chloroform are reported in the left panel of the following figure (a). All the electronic absorption spectra present an intense band associated with the HOMO-LUMO electronic transition. Its wavelength red shifts along with the increase in the conjugation length as a consequence of reducing the energy band. The wavelength maxima are, however, much lower than those observed for 2,5-di(alcoxy) phenyleneethynylene oligomers due to the electron-withdrawing character of the ester groups in the lateral chains. The maxima, however, are similar to those found for other (alkyl)benzoate PEs series, suggesting that the cholesteryl groups as lateral substituents have negligible effect on the

conjugation length at least in solution. The UV-Vis spectra of all the materials do not change with concentration or solvent excluding intramolecular aggregation. However when a di-polar solvent is used such as DMF, an absorption tail between 400 and 500 nm appears as evidence of aggregate formation, likely due to solvatochromic effects as proposed for polythiophenes and di(alkyl)-PPEs.

| <i>Molecule</i> | $\epsilon(M^{-1} cm^{-1}) 10^4$ | λ_{abs} (nm) | HHBW* (nm) | E_{S0-S1} (eV) | λ_{em} (nm) | Stokes shift (cm^{-1}) | $\Phi_F(\%)$ |
|--------------------|---------------------------------|-------------------------|---------------|---------------------|------------------------|-------------------------------|--------------|
| Trimer 12 | 7.97 | 344 | 66 | 3.42 | 370 | 2043 | 7 |
| Pentamer 14 | 14.25 | 364 | 68 | 3.14 | 405 | 2781 | 35 |
| Heptamer 17 | 13.74 | 372 | 85 | 3.05 | 417 | 2901 | 14 |
| Br-nPEBzCol | 10.79 | 380 | 111 | 3.02 | 422 | 2619 | 27 |
| Heptamer 15 | 62.55 | 374 | 73 | 3.09 | 413 | 2525 | 66 |
| oPE7 | 7.11 ^b | 374 | 73 | 3.08 | 414 | 2583 | 94 |

These polymers develop a new band coexisting with that in solution and corresponding to the absorption in the solid state (films) just after adding a non solvent such as methanol to the chloroform solutions. In this aggregate-induced band, according to Bunz, the ordering of the side chains affects the electronic properties of the conjugated chain substantially, however it can not be discarded that the strong π - π interaction give rise to a tight molecular package leading to a bathochromic shift. In our case, the absorption bands are broad in chloroform as is usually found for PPEs materials and may be attributed to the overlapping electronic transitions from different conformers in the ground state. The half height band width (HHBW) actually increases along the series, which is consistent with a larger number of conformers as the chain length increases.



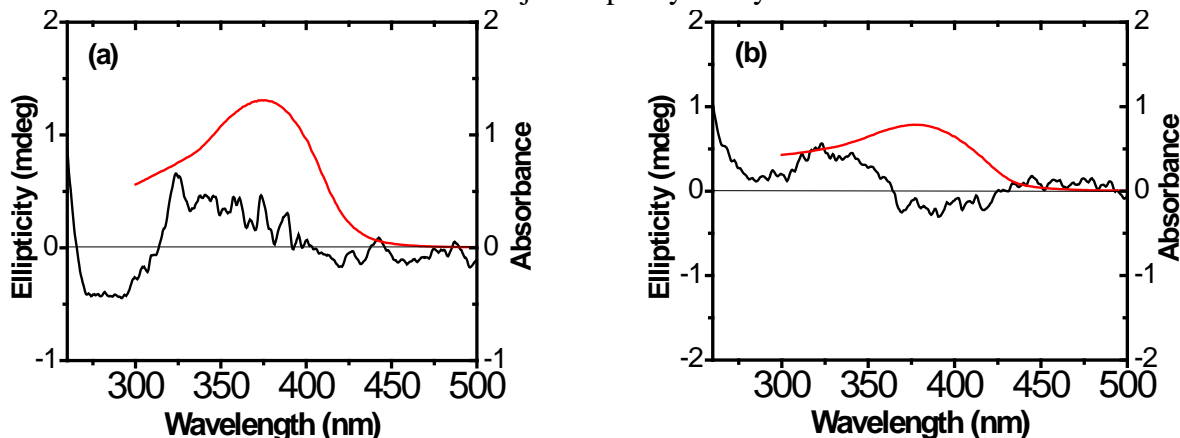
All the molecules emit in the high energy UV-blue region, with the first excited state energy obtained from the cross-over between the electronic absorption and emission spectra being around 3 eV. The first excited state energy decreases along the series in agreement with the higher electron delocalization. Accordingly, the maximum shifts from 370 nm to 422 nm in passing from the trimer to the polymer, see right panel of the above figure. The emission spectra are well resolved in contrast with the broad electronic absorption spectra. This behavior has been

attributed to the fact that these kinds of molecules assume a more planar conformation in the excited state with respect to the ground state. Particularly, in the cholesteryl PPEs, this assumption is supported by the following points: i) the emission spectrum does not change with excitation wavelength denoting the presence of only one emitting state as can be seen in Figure inserted on left side for the pentamer **14**, ii) the Stokes shift is in the range of values related to molecules that undergo conformational changes towards more planar geometry when passing from the ground to the excited state. We note a large increase of the Stokes shift from the trimer to the pentamer and heptamer that could be related to the increase in the half height width (HHBW), i.e., with longer oligomers, more conformers are possible in the ground state with stronger planarization occurring in the excited state; iii) the excitation spectrum matches the absorption spectrum and it does not change with the emission wavelength; this observation confirms that the stronger fluorescence peak and the lower energy shoulder are both associated with the same excited state.

In general, the fluorescence quantum yield, Φ_F , (table) is low without a noticeable trend in the series. Even though several ester substituted phenyleneethynylenes have been synthesized, little information is available in the literature on their optical properties, and particularly on fluorescence quantum yield. In one case, quantum yields of dialcoxy substituted phenyleneethynylenes were found to be in the range of 60%. The deviation from 100 % for those systems was demonstrated to be due mainly to intersystem crossing to triplet emitting states by photophysical and theoretical studies. In our case, the Stokes shift values are higher than those found for the dialcoxy PEs, suggesting that internal conversion is more likely to be important than in the ether series. Nevertheless, the fluorescence quantum yield of the (11-undecanol) benzoate PE heptamer (**oPE7**) is extremely high; almost 7 times that of the cholesteryl iodine terminated heptamer **17**, despite a Stokes shift of almost the same order of that of the **Br-nPEBzCol** polymer. This could suggest that the cholesteryl group favours intersystem crossing and triplet state formation; **oPE7** however has another structural difference relative to the homologue cholesteryl heptamer **15**, it terminates with H instead of iodine. The Φ_F of the H terminated cholesteryl heptamer **15** is indeed higher than that of **17** but still lower than that of **oPE7**, and supports the general remark on the cholesterol effects on the fluorescence quantum yield. The presence of the iodine for the oligomer series is responsible of further quenching of the fluorescence as previously found for 2,5-di(alcoxy) PE oligomers with halogens as terminal groups. The quenching effect of halogen is a well known effect as spin-orbit coupling promotes intersystem crossing.

Circular dichroism(CD) spectra down to 250 nm of the oligomer series dissolved in chloroform were collected. The OD at the absorption maximum was kept under 2 for all samples. All of the samples show some signal but the data are very noisy and have been smoothed using a 20 point smoothing function. The CD spectrum of **17** (Figure a) and **Br-nPEBzCol** (Figure b) are shown as examples along with the ground state absorption spectra. Compounds **12**, **14** and **17** all have weak positive CD associated with the UV absorption band. Similar weak positive dichroism has been observed in 5 α -cholestane-2 β ,3 β -diol bis (p-dimethylaminobenzoate), suggesting the

weak dichroism in **12**, **14** and **17** results from interaction between one phenyl acetylene unit and the chiral environment of the attached cholesterol unit. The polymer **Br-nPEBzCol** shows a negative Cotton effect at 375 nm and a positive Cotton effect at 325 nm. This (-/+) pattern gives evidence for interaction between two adjacent phenyl acetylene units.



Exciton chirality theory can be used to interpret this spectrum. Exciton chirality is defined as:

$R = \vec{R}_{ij} \cdot (\vec{\mu}_{i0} \times \vec{\mu}_{j0}) V_{ij}$, where \vec{R}_{ij} is the interchromophoric distance vector from transition dipole i to transition dipole j, $\vec{\mu}_{i0}$ and $\vec{\mu}_{j0}$ are electric transition dipole moments of excitation $0 \rightarrow a$ of groups i and j and V_{ij} is the interaction energy between the transition dipoles of groups i and j. The (-/+) pattern seen in the CD spectrum of the polymer shows $R < 0$. The quantity R is negative when there is left-handed screwness in the optically active compound and positive when there is right-handed screwness. An example of negative chirality in a cholesterol complex has been observed in 5 α -cholestane-2 β ,3 β -diol bis(p-dimethylaminobenzoate) where two chromophores are attached to the chiral center. The observation of negative chirality in the CD spectrum gives evidence that the polymer has long-range order leading to exciton coupling between the transition dipoles of adjacent monomer units. The weak CD signal suggests these materials are very floppy with stabilization energy greater than kT appearing only in the polymer.

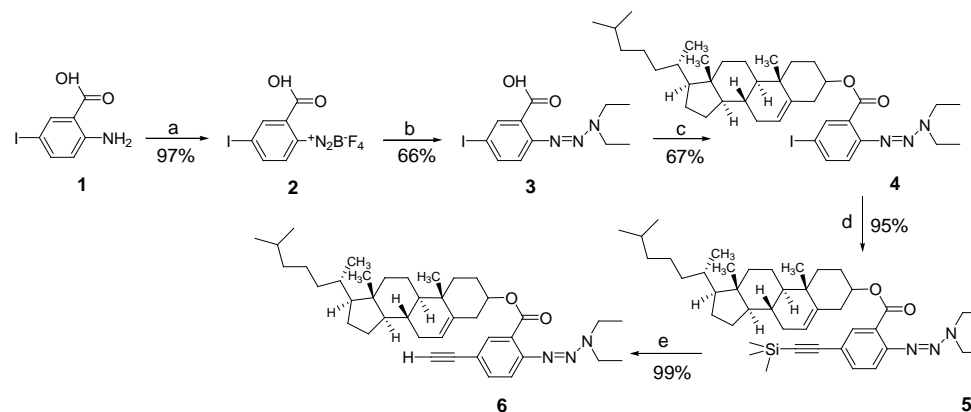
In conclusion, a series of benzoate phenyleneethynylene oligomers bearing cholesteryl as a solubilizing and mesogen group was bidirectionally synthesized giving rise to odd number oligomers, i.e., trimer, pentamer and heptamer just by applying two repetitive sets of reactions: involving palladium cross-couplings and iodinations at each cycle. According to X-ray diffraction studies, the molecules are self assembled in bilayers in a comb-like supramolecular assembly, which can be visualized as two back-to-back superposed combs, where the cholesteryl groups, which make up the tines or “teeth” of the comb, are oriented in opposite directions. The positional order within the lamellae is dependant on the oligomer’s length. For the trimer and heptamer, a Smectic A type mesophase is consistent with the data. For the heptamer and polymer, a rather Nematic type mesophase is favored. Since, the molecular shape of the materials resembles brick or board-like structures, and the molecules are stacked in blocks, these

(cholesteryl)benzoateethynylene materials could be named as Sanidic LCs as a general term to classify their mesomorphic behavior. The iodine terminal group has a significant noticeable effect on the structure and electronic optical properties of the oligomers by decreasing the quantum yields in solution. Weak circular dichroism signal suggests these oligomers are very floppy with long range order, while the polymer showing a negative Cotton effect at 375 nm and a positive Cotton effect at 325 nm gives evidence for exciton coupling between two adjacent phenyl acetylene units.

References: (a) M. Moroni, J. Le Moigne, S. Luzzati, *Macromolecules*, 1994, **27**, 562. (b) L. Kloppenburg, D. Jones, J.B. Claridge, H.C. Zur Loye, U.H.F. Bunz, *Macromolecules*, 1999, **32**, 4460. (c) U.H.F. Bunz, *Chem. Rev.*, 2000, **600**, 1605. (d) G. Castruita, E. Arias, I. Moggio, F. Pérez, D. Medellín, R. Torres, R. Ziolo, A. Olivas, E. Giorgetti, M. Muniz-Miranda, *J. Mol. Struct.*, 2009, **936**, 177. (e) V. James, P.K. Sudeep, C.H. Zurres, G.J. Thomas, *J. Phys. Chem. A*, 2006, **110**, 4329. (f) C.G. Swain, R. J. Rogers, *J. Am. Chem. Soc.*, 1975, **97** (4), 799. (g) M. George, R.G. Weiss, *Accounts of chemical research*, 2006, **39**, 489. and references therein. (h) K. Kubo, K. Tsuji, A. Mori, S. Ujhe, *J. Oleo Sci.*, 2004, **53**, 467. (i) I Dierking, *Textures of Liquid Crystals*, Wiley-VCH, Weinheim, 2003. (l) L. Kloppenburg, D. Jones, J.B. Claridge, H-C. Loye, U.H.F. Bunz, *Macromolecules*, 1999, **32**, 4460. (j) J.N. Wilson, P.M. Windscheif, U. Evans, M.L. Myrick, U.H.F. Bunz, *Macromolecules*, 2002, **35**, 8681. (k) E. Arias-Marin, J.C. Arnault, D. Guillon, T. Maillou, J. Le Moigne, B. Geffroy, J.M. Nunzi, *Langmuir*, 2000, **16**, 4309. (l) T. Miteva, L. Palmer, L. Kloppenburg, D. Neher, U.H.F. Bunz, *Macromolecules* 2000, **33**, 652. (m) I.B. Berlman, *Handbook of Fluorescence Spectra of Aromatic Molecules*, 2nd ed, Academic Press: London, New York, 1971. (n) J.R. Lakowicz, *Principles of fluorescence spectroscopy*, Kluwer Academia/Plenum Publishers 1999. (25) (o). S.-M. L. Chen, N. Harada, K. Nakanishi, *J. Am. Chem. Soc.*, 1974, **96**, 7352. (p) N. Harada, S.-M. L. Chen, K. Nakanishi, *J. Am. Chem. Soc.*, 1975, **97**, 5345. (q) N. Harada, K. Nakanishi, *Acc. Chem. Res.*, 1972, **5**, 257.

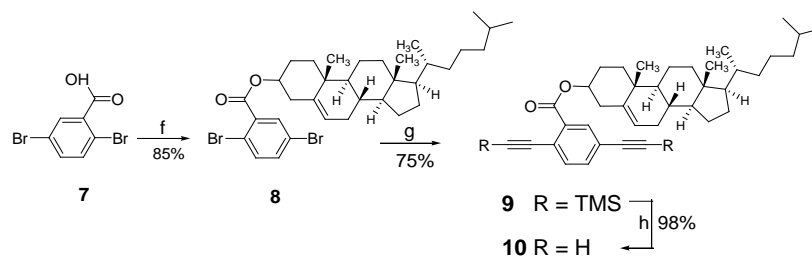
New Discoveries: there are no inventions to be patented as a result of this research grant. The results claimed that report new molecules are important for basic research. However the following full scientific paper was published: Synthesis, Optical and Structural Properties of Sanidic Liquid Crystal (Cholesteryl)benzoate-ethynylene Oligomers and polymer. Griselda Castruita, Vladimir García, Eduardo Arias, Ivana Moggio, Ronald Ziolo, Arturo Ponce, Virgilio González, Joy E. Haley, Jonathan L. Flikkema and Thomas Cooper. *J. Mater. Chem.***2012**, 22, 3770 DOI:10.1039/c2jm14918d.

Scheme 1



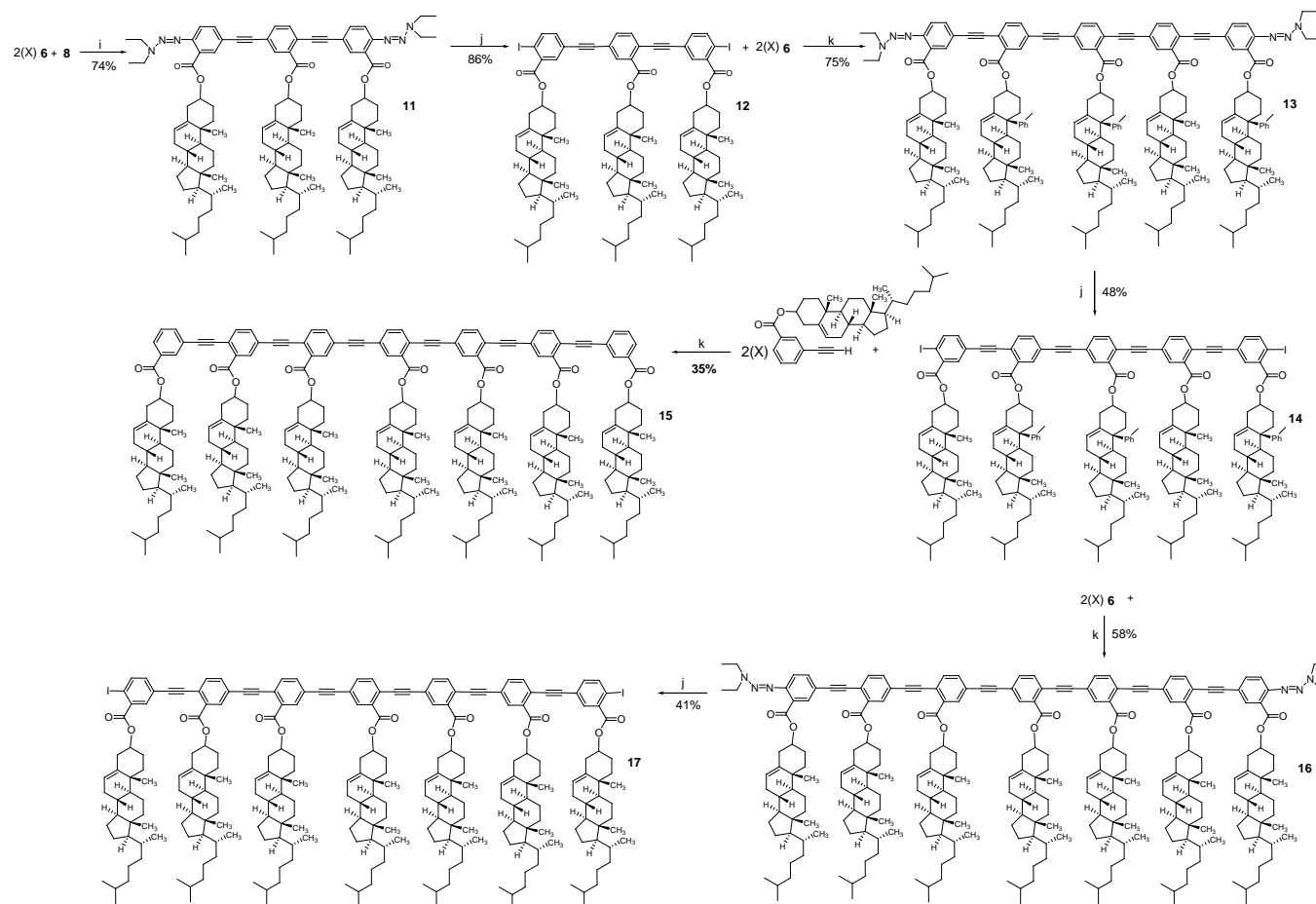
Reagents and conditions: (a) $\text{BF}_3 \cdot \text{OEt}_2$, tert-butyl- NO_2 , THF, -15°C , 2 h; (b) Et_2NH , K_2CO_3 , DMF, -10°C , 2 h; (c) cholesterol, DCC/DMAP, CH_2Cl_2 , 0°C , 15 h; (d) $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{PdCl}_2$ (2.5 % mol), CuI (1.5 % mol), TMSA, Et_3N , 60°C , 16 h; (e) TBAF, THF, r.t., 0.5 h.

Scheme 2



Reagents and conditions: (f) cholesterol, DCC/DMAP, CH_2Cl_2 , 0°C , 15 h; (g) $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{PdCl}_2$, CuI, TMSA, Et_3N , 60°C , 16 h; (h) TBAF, THF, r.t., 0.5 h.

Scheme 3



Reagents and conditions: (i) $[(C_6H_5)_3P]_2PdCl_2$ (2.5 % mol), CuI (1.5 % mol), TMSA, Et_3N , 60 °C, 16 h; (j) CH_3I , 120°C-vaccum, 15h; (k) $[(C_6H_5)_3P]_2PdCl_2$ (2.5 % mol), CuI (1.5 % mol), TMSA, Et_3N/THF , 60 °C, 16 h.